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Ab Initio Calculation of Vibrational Circular Dichroism Spectra Using Large Basis Set MP2 Force Fields

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1. INTRODUCTION

The prediction of the circular dichroism of the fundamental vibrational transitions of a chiral molecule at the harmonic level of approximation requires the implementation of (Stephens 1985, 1987)

$$R_i = \text{Im} [\langle 0 | \mu_{\text{el}} | 1 \rangle_i \cdot \langle 1 | \mu_{\text{mag}} | 0 \rangle_i] , \quad (1a)$$

$$\langle 0 | (\mu_{\text{el}})_\beta | 1 \rangle_i = \left(\frac{\hbar}{2\omega_i} \right)^{1/2} \sum_{\lambda, \alpha} P_{\alpha\beta}^\lambda S_{\lambda\alpha, i} , \quad (1b)$$

$$\langle 0 | (\mu_{\text{mag}})_\beta | 1 \rangle_i = - \left(2\hbar^3 \omega_i \right)^{1/2} \sum_{\lambda, \alpha} M_{\alpha\beta}^\lambda S_{\lambda\alpha, i} . \quad (1c)$$

R_i is the rotational strength of the fundamental excitation of the i th normal mode of energy $\hbar\omega_i$. The corresponding normal coordinates, Q_i , are related to Cartesian nuclear displacement coordinates $X_{\lambda\alpha}$ (λ = nucleus, α = x,y,z) via

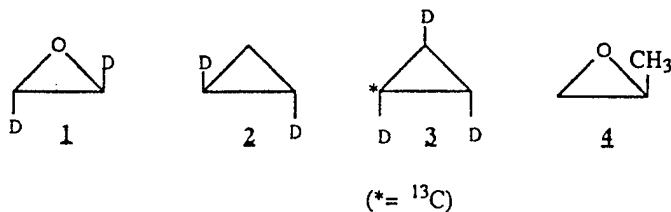
$$X_{\lambda\alpha} = \sum_i S_{\lambda\alpha, i} Q_i . \quad (2)$$

The electric and magnetic dipole transition moments, whose scalar products determine rotational strengths, are in turn a function, respective, of the tensors, $P_{\alpha\beta}^\lambda$ and $M_{\alpha\beta}^\lambda$. The tensors $P_{\alpha\beta}^\lambda$, which determine electric dipole transition moments, are the well-known atomic polar tensors (APTs) (Stephens et al. 1990). The tensors $M_{\alpha\beta}^\lambda$, which determine magnetic dipole transition moments, are the atomic axial tensors (AATs), more recently introduced into the literature (Stephens 1985, 1987; Stephens et al. 1990).

Since the development of equation (1c) for vibrational magnetic dipole transition moments, a substantial number of predictions of vibrational circular dichroism (VCD) spectra utilizing equation (1) and ab initio SCF or post-SCF calculations of APTs and AATs have been published. For some molecules,

predictions have been compared to experimental data (see, for example, Lowe, Stephens, and Segal 1986; Jalkanen et al. 1987, 1988, 1989, 1990; Kawiecki et al. 1988, 1991; Bursi, Devlin, and Stephens 1990; Lowe and Alper 1988; Dothe, Lowe, and Alper 1988; Amos, Handy, and Palmieri 1990; Malon et al. 1992; Fablioni et al. 1993). Unfortunately, these predictions have used vibrational force fields of widely differing provenance, reliability, and accuracy. The accuracy of predicted VCD intensities has therefore been limited not only by errors in the APTs and AATs but also by errors in vibrational frequencies and normal coordinates. Unambiguous attribution of the origins of differences between predicted and observed VCD spectra has thus been impossible.

Accurate harmonic vibrational force fields, frequencies, and normal coordinates require *ab initio* calculations at the post-SCF level. Of the various approaches to the inclusion of correlation in the calculation of harmonic force fields, Møller-Plesset second-order perturbation theory (MP2) has been the most widely used. When large basis sets are used, MP2 force fields typically yield harmonic frequencies in error by only 1%–3% (Simandiras et al. 1988). Anharmonicity corrections to vibrational frequencies are then comparable to or larger than errors in harmonic frequencies. Calculations of vibrational spectra using such force fields should not be significantly limited in accuracy by residual errors in harmonic frequencies. Of course, large basis set MP2 calculations of harmonic force fields are computationally demanding. However, recent advantages in the computation of MP2 second derivatives via analytical derivative methods (Stanton, Gauss, and Bartlett 1992; Gauss, Stanton, and Bartlett 1992; Trucks et al. unpublished)* have greatly enlarged the range of molecules for which such calculations are feasible. As a result, large basis set MP2 calculations for chiral molecules whose VCD spectra have been measured experimentally are now practicable. We here report calculations of VCD spectra which take advantage of this development. The following molecules have been studied:



MP2 force fields have been calculated using a [5s4p2d/3s2p] (TZ/2P [Stephens et al. 1990]) basis set. APTs and AATs have also been calculated using this basis set. The results are compared to existing VCD spectra and to rotational strengths obtained thence. For 1-3 the sensitivity of the results to further

* See GAUSSIAN 92 user's manual.

enlargement of the basis set to the [8s6p3d/6s3p] (VD/3P [Stephens et al. 1990]) level has also been examined.

The VD/3P calculations for **1** were reported in a prior communication (Stephens et al. 1993).

2. METHODS

Ab initio calculations have been carried out using Cray-YMP versions of CADPAC 4.0 and 5.0 and Cray-YMP and Cray-2 versions of GAUSSIAN 92. MP2 Hessians and APTs were calculated at the TZ/2P basis set level for oxirane (**5**) and cyclopropane (**6**) using 'conventional' methods and CADPAC 4.0 and for propylene oxide (**4**) using semidirect methods and GAUSSIAN 92; the latter were also used for calculations on **5** and **6** at the VD/3P basis set level. SCF APTs were calculated for each molecule at all basis set levels using CADPAC 4.0 or 5.0. AATs were calculated about an origin O using the distributed origin (DO) gauge (Stephens 1987; Stephens et al. 1990) when

$$\left(M_{\alpha\beta}^{\lambda}\right)^0 = \left(I_{\alpha\beta}^{\lambda}\right)^{\lambda} + \frac{i}{4\hbar c} \sum_{\gamma\delta} \epsilon_{\beta\gamma\delta} R_{\lambda\gamma}^0 P_{\alpha\delta}^{\lambda}, \quad (3)$$

where R_{λ}^0 is the equilibrium position of nucleus λ , and $(I_{\alpha\beta}^{\lambda})^{\lambda}$ is the electronic AAT of nucleus λ obtained with the coordinate origin at R_{λ}^0 . The 'local' AATs, $(I_{\alpha\beta}^{\lambda})^{\lambda}$, were calculated at the SCF level using CADPAC 4.0 or 5.0 via the relation (Stephens et al. 1990)

$$(I_{\alpha\beta}^{\lambda})^{\lambda} = (I_{\alpha\beta}^{\lambda})^0 - \frac{i}{4\hbar c} \sum_{\gamma\delta} \epsilon_{\beta\gamma\delta} R_{\lambda\gamma}^0 E_{\alpha\delta}^{\lambda}(\pi), \quad (4)$$

where $(I_{\alpha\beta}^{\lambda})^0$ is the electronic AAT obtained with the origin at 0 and $E_{\alpha\beta}^{\lambda}(\pi)$ is the electronic APT calculated using the momentum representation (Stephens et al. 1990). SCF and 'semi-MP2' DO gauge AATs were then obtained by combining SCF local AATs and either SCF or MP2 APTs respectively using equation (3). Vibrational frequencies and normal coordinates were obtained from the appropriately mass-weighted Hessian. Rotational strengths were obtained from equation (1). Note that the use of the DO

gauge in the calculation of AATs guarantees origin-independent rotational strengths (as long as the same APTs are used in equation (3) as in equation [1b]). Dipole strengths, defined by

$$D_i = |\langle 0 | \mu_{el} | 1 \rangle_i|^2, \quad (5)$$

were simultaneously calculated via equation (1b). Calculated frequencies, dipole strengths, and rotational strengths have been used to synthesize unpolarized absorption and VCD spectra using Lorentzian band shapes (Kawiecki et al. 1988).

3. RESULTS AND DISCUSSION

Experimental solution unpolarized absorption and VCD spectra of 1–4 (Kawiecki et al. 1991; Freedman et al. 1991a, 1991b; Freedman et al. unpublished) in C-H stretching, C-D stretching, and mid-IR spectral regions are reproduced in Figures 1–4. Mid-IR spectra have not yet been reported for 3.

Frequencies, dipole strengths, and rotational strengths calculated using TZ/2P MP2 force fields and APTs and TZ/2P semi-MP2 AATs for 1–4 are given in Tables 1–4. Unpolarized absorption and VCD spectra derived thence are plotted in Figures 1–4.

Comparison of calculated and experimental unpolarized absorption and VCD spectra leads to unambiguous assignments of the fundamental bands of 1, 2, and 4 in the mid-IR regions and of 1–3 in the C-H and C-D stretching regions. The frequencies, dipole strengths, and rotational strengths reported (Kawiecki et al. 1991; Freedman et al. 1991a, 1991b; Freedman et al. unpublished) for these bands are listed in Tables 1–4. Assignment of the C-H stretching spectra of 4 is less straightforward. Only one of the fundamentals can be confidently assigned; its experimental frequency, dipole strength, and rotational strength are given in Table 4.

Analogous calculations have also been carried out for 1–3 using the VD/3P basis set. The results are given in Tables 1–3 and plotted in Figures 1–3. All VD/3P results are qualitatively identical to those obtained at the TZ/2P basis set level. They require no changes in the assignments of the spectra of 1–3.

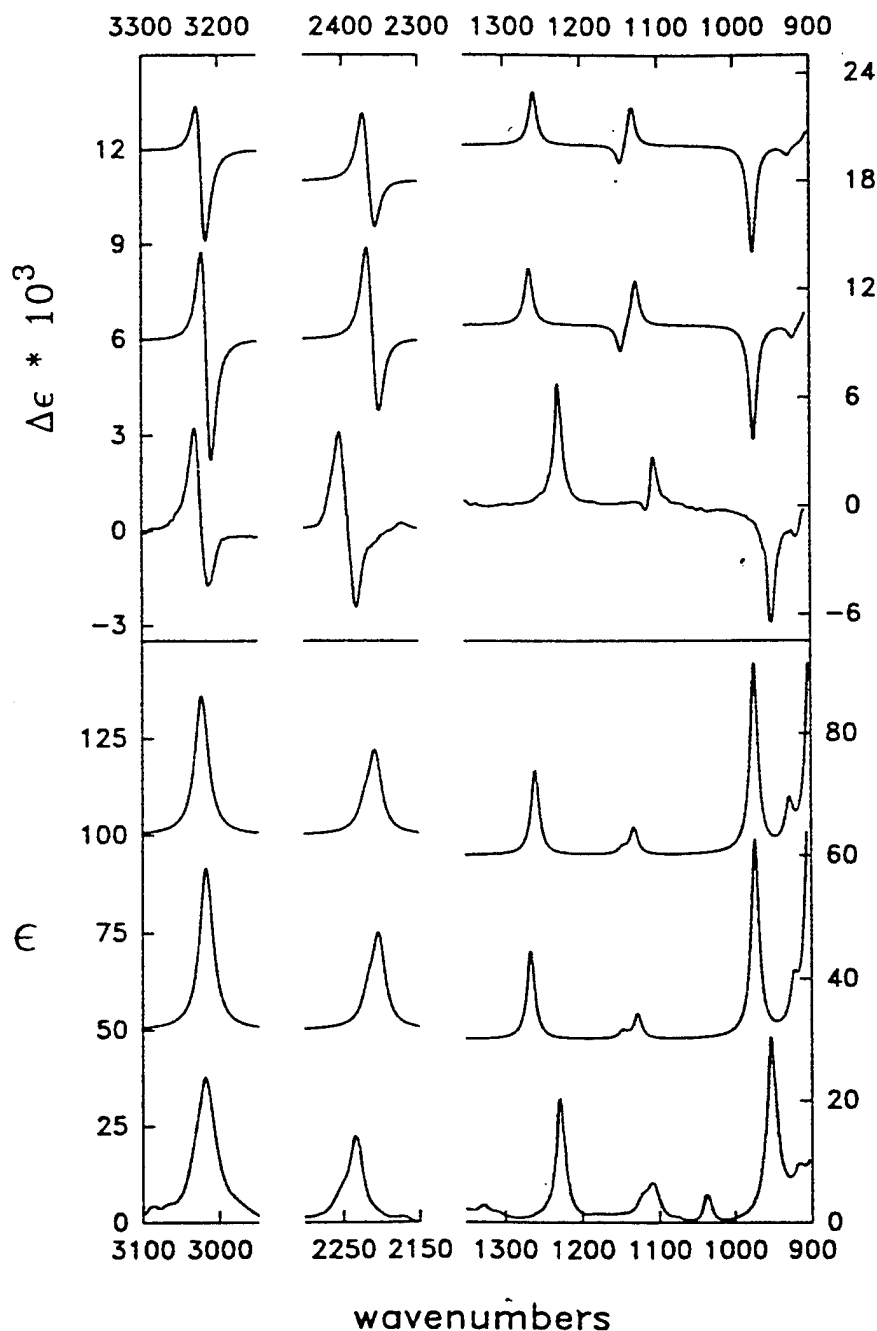


Figure 1. Predicted and experimental unpolarized absorption and VCD spectra of 1. Upper and middle spectra are predicted using TZ/2P and VD/3P basis sets respectively; half widths and half height of the Lorentzian bands (γ) are 6.0 cm^{-1} (mid-IR region) and 10.0 cm^{-1} (C-H/C-H stretching regions). Lower spectra are the experimental spectra of Freedman et al. (1991a) in CS_2 (mid-IR region) and C_2Cl_4 (C-H/C-D stretching regions); note that absorption at $1,034$ and $1,117 \text{ cm}^{-1}$ is attributed to impurities. VCD spectra are for (2S, 3S)-1. Upper and lower frequency scales apply to calculated and experimental spectra respectively. Left and right vertical scales apply to C-H/C-D stretching and mid-IR spectra respectively.

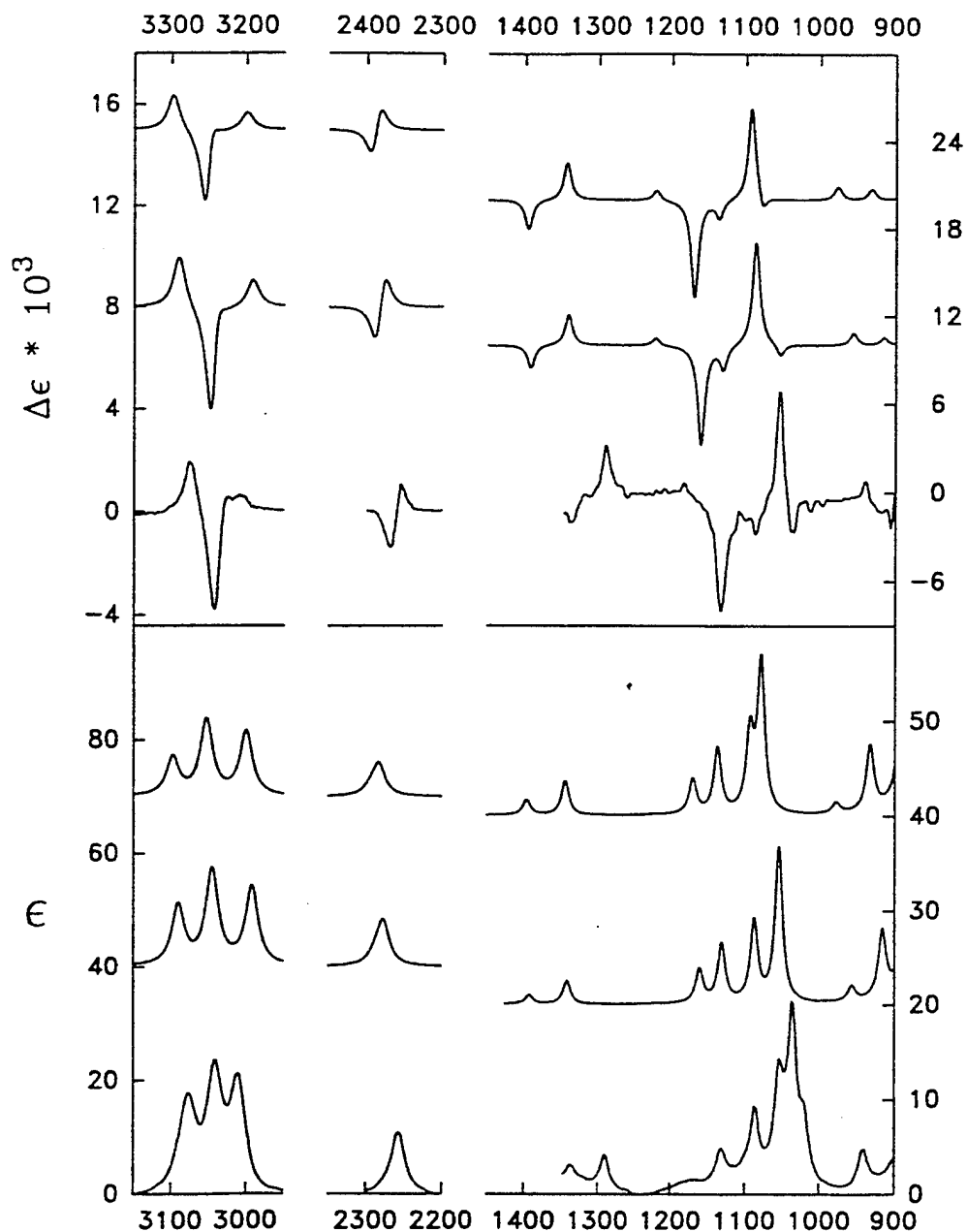


Figure 2. Predicted and experimental unpolarized absorption and VCD spectra of 2. Upper and middle spectra are predicted using TZ/2P and VD/3P basis sets respectively; γ is 6.0 cm^{-1} and 10.0 cm^{-1} in the mid-IR and C-H/C-D stretching regions respectively. Lower spectra are the experimental spectra of Freedman et al. (unpublished) in CS_2 (mid-IR region) and C_2Cl_4 (C-H/C-D stretching regions). VCD spectra are for (1S, 2S)-2. Upper and lower frequency scales apply to calculated and experimental spectra respectively. Left and right vertical scales apply to C-H/C-D stretching and mid-IR spectra respectively.

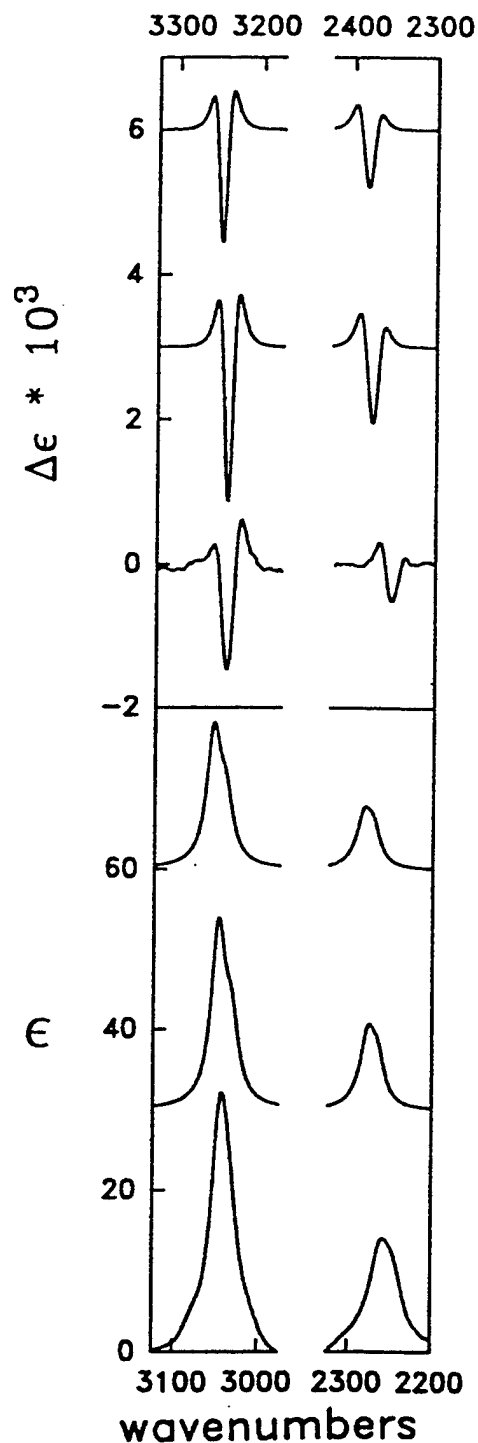


Figure 3. Predicted and experimental unpolarized absorption and VCD spectra of 3. Upper and middle spectra are predicted using TZ/2P and VD/3P basis sets respectively; $\gamma = 10.0 \text{ cm}^{-1}$. Lower spectra are the experimental spectra of Freedman et al. (1991b) in C_2Cl_4 . VCD spectra are for (2S, 3S)-3. Upper and lower frequency scales apply to calculated and experimental spectra respectively.

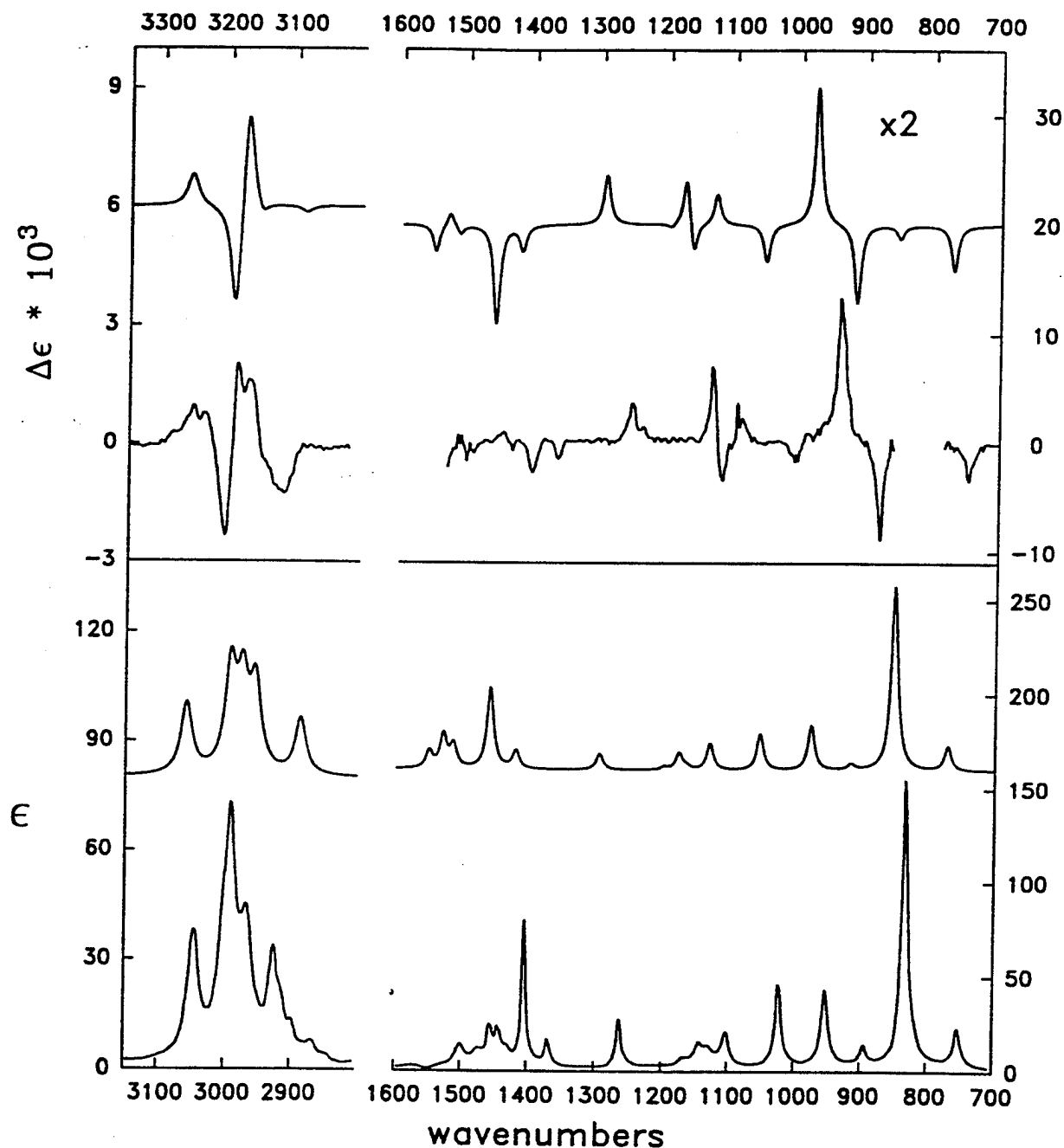


Figure 4. Predicted and experimental unpolarized absorption and VCD spectra of 4. Upper spectra are predicted using the TZ/2P basis sets; γ is 6.0 and 10.0 cm^{-1} in the mid-IR and C-H stretching regions respectively. Lower spectra are the experimental spectra of Kawiecki et al. (1991) in CS_2 and CCl_4 . VCD spectra are for (S)-4. Upper and lower frequency scales apply to calculated and experimental spectra respectively.

Table 1. Frequencies, Dipole Strengths, and Rotational Strengths of Molecule 1^a

$\bar{\nu}$			D				R			
calc.		exp. ^b	calc.			exp. ^b	calc.			exp. ^b
TZ/2P	VD/3P		MP2 ^c		SCF ^d		MP2 ^c		SCF ^d	
			TZ/2P	VD/3P ^g	TZ/2P	VD/3P	TZ/2P	VD/3P ^g	TZ/2P	VD/3P
3223	3218	3027	27.2	31.0	27.2	31.0	22.8	(15.7)	21.0	29.1
3219	3213	3014	5.9	7.4	6.2	7.4	-24.4	(-18.2)	-19.5	-25.0
2371	2367	2252	6.9	8.6	7.7	9.0	12.7	(9.2)	10.4	13.7
2358	2353	2232	24.6	27.7	43.7	45.9	-11.2	(-7.4)	-9.9	-14.1
1443	1440		8.0	8.4	12.1	12.6	-8.3	(-7.4)	-9.0	-10.4
1381	1380		0.4	0.6	1.0	1.1	-1.3	(-1.2)	-2.0	(-15)
1260	1266	1226	19.1	19.7	25.6	26.6	10.9	(10.2)	10.9	(-2.5)
1147	1147	1109	1.5	1.9	0.6	0.1	-6.3	(-5.9)	3.1	24.1
1132	1128	1102	6.6	6.3	9.9	11.1	10.1	(9.0)	7.8	-4.9
974	973	948	54.7	57.1	108.1	108.2	-28.2	(-26.5)	-35.1	11.1
928	923	914	12.3	11.9	20.2	20.1	-26.7	(-3.0)	0.1	-29.0
898	900		123.6	122.8	195.9	192.0	-3.6	(8.5)	7.6	-6.2
830	820		32.1	38.7	51.8	59.3	8.0	(0.7)	-0.1	(~+5)
770	775		110.4	113.9	142.8	148.2	1.7	(10.5)	12.2	(+)
672	675		1.1	0.8	1.5	1.5	11.8	(0.1)	0.8	0.6

^a Frequencies, $\bar{\nu}$, in cm^{-1} ; dipole strengths, D, in $10^{-40} \text{ esu}^2 \text{ cm}^2$; rotational strengths, R, in $10^{-44} \text{ esu}^2 \text{ cm}^2$. Rotational strengths are for the (2S, 3S) enantiomer.

^b From Freedman et al. (1991a); in C_2Cl_4 solution for C-H and C-D stretching modes and in CS_2 solution otherwise; values in parentheses estimated from gas phase data. Rotational strengths were not normalized to 100% enantiomeric excess (ee); ee for (2S, 3S)-1 and (2R, 3R)-1 were estimated to be 94%.

^c Calculated using MP2 APTs.

^d Calculated using SCF APTs.

^e Calculated using MP2 APTs and semi-MP2 AATs.

^f Calculated using SCF APTs and AATs.

^g Numbers in parentheses are obtained using TZ/2P APTs and AATs.

Table 2. Frequencies, Dipole Strengths, and Rotational Strengths of Molecule 2^a

$\bar{\nu}$			D					R				
calc.		exp. ^b	calc.			exp. ^b		calc.			exp. ^b	
TZ/2P	VD/3P		MP2		SCF			MP2		SCF		
			TZ/2P	VD/3P	TZ/2P	VD/3P		TZ/2P	VD/3P	TZ/2P	VD/3P	
3298	3290	3076	5.8	9.2	20.9	25.7	19	3.2	4.7	5.6	7.6	4.8
3253	3245	3041	10.1	13.0	30.1	32.9	25	-16.6	-21.8	-29.6	-35.8	-9.9
3250	3242	3035	1.7	2.0	4.5	4.7		12.0	14.8	21.3	24.3	4.4
3200	3192	3012	10.1	12.5	26.6	29.2	21	1.6	2.5	2.8	4.1	1.4
2394	2388	2270	1.4	1.8	4.2	4.7		-4.4	-6.1	-8.7	-10.8	-3.7
2383	2377	2257	6.7	9.4	22.0	25.2	15	4.1	5.8	8.3	10.3	3.3
1517	1510		1.7	1.0	0.8	0.5		0.9	0.6	0.6	0.4	
1396	1392	1338	2.0	1.2	1.2	0.8	8.4	-6.4	-4.9	-4.7	-3.9	-7.7
1344	1342	1290	4.7	3.2	3.0	2.3	6.8	8.3	6.8	6.3	5.5	10.2
1221	1222	1180	0.1	0.1	0.1	0.1		2.5	1.9	2.0	1.6	3.0
1169	1160	1134	5.4	5.3	4.0	4.2	13	-25.0	-25.4	-20.2	-21.8	-42.6
1136	1130	1087	10.5	9.6	6.7	6.9	21	-4.8	-6.1	-3.7	-5.1	-13.3
1093	1087	1052	12.8	13.6	9.2	10.7	23	25.8	28.6	21.0	24.6	28.2
1078	1054	1037	25.5	27.0	15.4	18.4	38	-4.7	-3.5	-3.6	-2.8	-15.9
977	956	942	2.0	2.9	0.0	0.3	15	4.0	3.8	0.5	1.3	5.5
932	916		12.7	13.3	29.4	28.6		3.4	2.5	5.0	3.5	
882	877		85.7	80.8	107.0	101.7		6.3	5.2	6.6	5.5	
806	802		78.3	75.6	80.1	77.2		-12.2	-11.1	-11.8	-10.8	
746	740		8.6	7.6	8.7	8.3		1.8	2.1	2.0	2.3	
640	638		4.2	4.1	3.3	3.4		0.0	-0.8	-0.1	-0.7	
628			1.3	1.2	0.9	0.8		0.2	0.6	0.1	0.5	

^a Definitions and units as in Table 1. Rotational strengths are for the (1S, 2S)-enantiomer.^b From Freedman et al. (unpublished); in C₂Cl₄ for C-H and C-D stretching modes and in CS₂ solution otherwise. Rotational strengths were not normalized to 100% ee; ee for (1R, 2R)-2 and (1S, 2S)-2 were estimated to be >98%.

Table 3. Frequencies, Dipole Strengths, and Rotational Strengths of Molecule 3^a

$\bar{\nu}$			D, calc.				R			
calc.		exp. ^b	MP2		SCF		calc.		exp. ^b	
TZ/2P	VD/3P		TZ/2P	VD/3P	TZ/2P	VD/3P	MP2	VD/3P		
3255	3248	3054	12.9	17.8 (12.7)	40.3	46.4	6.9	7.8 (6.1)	12.3	12.8
3250	3242	3041	1.6	1.9 (1.5)	4.2	4.4	-10.6	-12.6 (-9.9)	-18.9	-20.7
3240	3231	3025	6.1	7.7 (6.2)	16.6	18.2	3.7	4.8 (3.8)	6.6	7.9
2396	2390	2271	0.5	0.7 (0.5)	1.6	1.8	2.2	2.8 (2.0)	4.3	5.1
2383	2377	2258	6.9	9.8 (6.9)	22.4	26.2	-4.1	-5.3 (-3.8)	-8.1	-9.4
2372	2366	2245	5.0	6.5 (4.9)	15.6	16.9	1.9	2.4 (1.7)	3.8	4.3
1416	1409	1348	0.1	0.1 (0.1)	0.1	0.1	1.0	1.0 (1.1)	1.0	1.0
1349	1347	1302	3.8	2.5 (4.2)	2.3	1.7	-3.0	-2.5 (-3.1)	-2.4	-2.2
1339	1337	1290	4.7	3.0 (5.0)	2.9	2.1	2.2	1.8 (2.3)	1.6	1.4
1201	1201	1163	3.4	2.8 (3.0)	2.6	2.3	-2.9	-2.6 (-2.6)	-2.8	-2.7
1121	1112	1074	21.1	23.6 (24.6)	13.9	17.5	-0.3	0.0 (0.0)	-0.2	0.1
1112	1099	—	4.7	1.8 (2.2)	3.6	1.6	1.3	0.6 (0.6)	0.8	0.3
1077	1069	1037	14.5	14.6 (15.3)	9.3	10.7	1.5	2.0 (1.9)	1.7	2.1
959	941		2.5	2.1 (2.2)	6.4	5.3	2.3	2.0 (2.0)	3.3	2.8
936	917		0.8	0.8 (0.8)	6.8	6.0	-1.5	-1.4 (-1.5)	-2.3	-2.0
895	881		14.9	16.2 (16.1)	29.6	29.8	1.4	1.5 (1.6)	1.4	1.5
841	838		92.5	90.7 (92.7)	103.0	100.9	-2.2	-2.3 (-2.4)	-2.2	-2.4
774	769		74.0	71.2 (72.8)	73.6	70.7	0.1	0.0 (0.1)	0.1	0.0
694	688		3.1	2.1 (3.0)	2.5	2.2	0.1	0.1 (0.1)	0.1	0.1
610	608		0.2	0.2 (0.3)	0.1	0.1	0.0	0.0 (0.0)	0.0	0.0
595	593		5.6	5.6 (5.8)	4.8	4.9	0.0	0.1 (0.0)	0.0	0.1

^a Definitions and units as in Table 1. Rotational strengths are for the (2S, 3S)-enantiomer.

^b From Freedman et al. (1991b); in C₂Cl₄ solution for C-H and C-D stretching modes and in CS₂ solution otherwise. Rotational strengths were not normalized to 100% ee.

Table 4. Frequencies, Dipole Strengths, and Rotational Strengths of Molecule 4^a

$\bar{\nu}$		D			R		
calc. TZ/2P	exp. ^b	calc.		exp. ^b	calc.		exp. ^b
		MP2 TZ/2P	SCF TZ/2P		MP2 TZ/2P	SCF TZ/2P	
3259	3047	17.3	29.8	29.9	1.9	2.2	3.5
3193	—	25.2	55.1	—	-7.1	-8.0	—
3175	—	15.9	30.7	—	16.9	29.0	—
3174	—	4.8	12.3	—	-10.0	-19.3	—
3156	—	21.5	34.1	—	-1.0	-1.4	—
3087	—	14.6	26.5	—	-0.4	-0.6	—
1550	1500	10.0	12.0	15.1	-3.5	-4.5	-4.0
1529	1456	19.9	15.4	16.0	1.8	1.4	—
1514	1444	14.1	10.2	14.0	-1.2	-1.1	—
1458	1406	51.4	46.1	52.5	-13.4	-13.2	-8.4
1420	1369	11.8	14.3	14.7	-3.5	-4.4	-3.3
1295	1262 ^c	11.4	14.1	25.7 ^c	7.6	7.5	15.6 ^c
1199	1165	2.3	4.0	4.2	-0.7	-1.8	-0.4
1177	1143	13.0	20.5	13.1	8.5	9.6	21.4
1165	1130	2.5	3.6	13.9	-5.9	-0.8	-15.9
1130	1103	21.6	34.7	26.5	5.4	9.3	8.1
1054	1022	31.5	36.6	56.1	-7.1	-8.3	-6.7
977	951	41.9	66.1	65.9	28.1	35.5	71.9
916	893	5.8	15.0	19.4	-17.1	-24.7	-42.8
852	829 ^c	199.2	312.6	287.6 ^c	-3.1	-2.2	—
771	748 ^c	28.5	46.8	40.9 ^c	-11.7	-15.2	-21.6 ^c
407	414	42.7	52.3		3.8	4.5	
371	373	46.4	59.9		11.9	15.4	
219	200 ^d	8.1	10.6		-3.5	-3.7	

^a Definitions and units as in Table 1. Rotational strengths are for the (S) enantiomer.

^b From Kawiecki et al. (1991); in CCl₄ solution, except where indicated. Rotational strengths were not normalized to 100% ee.

^c CS₂ solution data.

^d Gas-phase data.

Calculated TZ/2P vibrational frequencies are in excellent qualitative agreement with experiment for all assigned fundamentals of 1–4. Calculated frequencies are greater than experimental frequencies, with the exception of two low frequency modes of 4. The ranges/averages of the (absolute) differences are: 1) 1.5%–6.8%/4.1%, 2) and 3) 3.1%–7.2%/5.0%, and 4) 0.5%–7.0%/3.6%. For the mid-IR modes alone the ranges/averages are: 1) 1.5%–3.4%/2.6%, 2) and 3) 3.1%–5.0%/3.9%, and 4) 0.5%–5.0%/3.2%. For the C-H and C-D stretching modes alone, the ranges/averages are: 1) 5.3%–6.8%/6.1%, 2) and 3) 5.5%–7.2%/6.3%, and 4) 7.0%–7.0%. Calculated VD/3P MP2 frequencies for 1–3 are very close to the TZ/2P MP2 frequencies. The maximum/average differences are: 1) 1.2%/0.3%, 2) and 3) 2.2%/0.7%. The differences between calculated and experimental frequencies are very little altered. For 1–3, a very large ($\approx 50\%$) increase in the basis set size above the TZ/2P level thus yields insignificant improvement.

The differences between experimental and calculation frequencies can be attributed to residual errors in the calculated harmonic frequencies and to the contributions of anharmonicity and solvent effects to the experimental frequencies. A comparison of calculated TZ/2P MP2 and experimentally derived harmonic frequencies for several small molecules found differences averaging 2.2% (Simandiras et al. 1988). Gas phase and solution frequencies reported for 1 (Freedman et al. 1991a) and 2 (Freedman et al. unpublished) differ on average by 0.4% and 0.6% respectively. We therefore conclude that anharmonicity is overall the dominant contributor to the differences in calculated and experimental frequencies for 1–4. This conclusion is consistent with known anharmonicity contributions to experimental frequencies for other small molecules (Hehre et al. 1986).

Dipole strengths calculated at the TZ/2P basis set level are in excellent qualitative agreement with experimental dipole strengths for all assigned fundamentals of 1–4, demonstrating the substantial accuracy of both the harmonic normal coordinates and the APTs. In 1–3, dipole strengths are very little changed on expansion of the basis set to the VD/3P level, indicating substantial basis set saturation in the TZ/2P APTs.

Quantitative comparison of calculated and experimental dipole strengths is complicated by the absence of well-defined error bars on experimental dipole strengths, which were obtained by fitting of absorption spectra using analytical band shape functions. The dipole strengths of weak bands and of poorly resolved bands are particularly uncertain. Undoubtedly, a significant fraction of the difference between calculated and experimental dipole strengths is attributable to experimental error. On the other hand, errors in calculated dipole strengths arising from residual errors in normal coordinates and APTs and from the

absence of anharmonicity and condensed phase effects can all be expected to contribute significantly. Comparison of the dipole strengths of the d_0 - and d_4 -isotopomers of **1**, calculated at the VD/3P MP2 level, to accurate gas phase experimental values demonstrated (Stephens et al. 1993) that 1) with the exception of C-H and C-D stretching modes, calculated dipole strengths agreed with experimental values within experimental error while, 2) in the case of C-H and C-D stretching modes, agreement was significantly worse. Errors arising from errors in the harmonic force field and APTs and from the absence of anharmonicity thus appear to be small except in hydrogenic stretching modes, where anharmonicity is more significant. Given the small differences in dipole strengths of **1–3** at the TZ/2P and VD/3P levels, it can then be inferred that, for **1–4** at both TZ/2P and VD/3P levels: 1) in the mid-IR region the dominant contributions to the differences in calculated and experimental dipole strengths are condensed phase effects and experimental errors and 2) anharmonicity is also likely to contribute significantly in the C-H and C-D stretching regions.

Rotational strengths calculated at the TZ/2P basis set level are in excellent qualitative agreement with experimental rotational strengths for all assigned fundamentals of **1–4**. In particular, all signs are correctly predicted. The substantial accuracy of the MP2 force field and APTs is further confirmed. In addition, the substantial accuracy of the semi-MP2 AATs is demonstrated. In **1–3**, rotational strengths are very little changed on expansion of the basis set to the VD/3P level, with the exception of the C-H and C-D stretching modes. For the mid-IR modes, basis set saturation appears to be comparable to that of the dipole strengths; for the C-H and C-D stretching modes it is somewhat less. The difference must be attributed to a lesser degree of basis set saturation of the AATs than of the APTs. This conclusion is confirmed by calculations of dipole and rotational strengths using VD/3P force fields and TZ/2P APTs and AATs (Tables 1–3).

As are dipole strengths, experimental rotational strengths are obtained by fitting of VCD spectra using analytical band shape functions. However, the quantitative accuracy of experimental rotational strengths is substantially less well-defined than that of dipole strengths since experimental VCD spectra are less accurate than unpolarized absorption spectra (Nafie 1988; Keiderling 1990). Resolution is lower. Signal-to-noise ratio is much worse. Absolute calibration is less straightforward and reliable. Artifactual signals are difficult to eliminate. It is consequently very difficult to quantify the contributions of experimental error to the differences between calculated and experimental rotational strengths.

Theoretical errors are also hard to quantitate. Errors in the harmonic force field and APTs are undoubtedly insignificant relative to errors in the AATs. The predominant deficiency in the AATs is the incomplete inclusion of correlation as a result of the calculation of the local AATs at only the SCF level. In the case of the TZ/2P calculations, as discussed previously, some basis set error is also present. An estimate of the overall sensitivity of rotational strengths to the inclusion of correlation in the AATs can be obtained by eliminating correlation contributions to the APTs. Rotational strengths obtained using SCF APTs and AATs are given in Tables 1–4. The (absolute) changes in rotational strengths for those bands of 1–4 for which experimental rotational strengths are available average $2.9 \times 10^{-44} \text{ esu}^2 \text{ cm}^2$ at the TZ/2P basis set level. The differences between rotational strengths calculated using TZ/2P MP2 APTs and semi-MP2 AATs and experimental rotational strengths average $6.4 \times 10^{-44} \text{ esu}^2 \text{ cm}^2$. It is therefore reasonable to conclude that a significant fraction of residual differences between calculated and experimental rotational strengths can be attributed to the incomplete inclusion of correlation in the calculation of AATs.

Our calculations do not successfully reproduce the C-H stretching VCD of 4. This could be attributed to residual errors in our harmonic calculations or to anharmonicity (Fermi resonance). In view of the obvious complexity of the C-H stretching absorption spectrum, the latter is almost certainly the principal contributor.

A number of calculations of rotational strengths for 1–4 have previously been reported (Lowe, Stephens, and Segal 1986; Jalkanen et al. 1988, 1989, 1990; Kawiecki et al. 1988, 1991; Lowe and Alper 1988; Fablioni 1993; Freedman et al. 1991b; Stephens, Jalkanen, and Kawiecki 1990; Dutler and Rauk 1989; Rauk and Yang 1992; Yang and Rauk 1992; Polavarapu and Bose 1990, 1991; Freedman and Nafie 1988). These calculations have used a variety of harmonic force fields; *ab initio* SCF (Fablioni et al. 1993; Dutler and Rauk 1989; Rauk and Yang 1992; Yang and Rauk 1992; Polavarapu and Bose 1990, 1991), empirically scaled *ab initio* SCF (scaled quantum mechanical [SQM]) (Lowe, Stephens, and Segal 1986; Jalkanen et al. 1988, 1989; Kawiecki et al. 1988, 1991; Lowe and Alper 1988; Stephens, Jalkanen, and Kawiecki 1990; Freedman and Nafie 1988) and empirical general valence (Jalkanen et al. 1990; Stephens, Jalkanen, and Kawiecki 1990; Polavarapu and Bose 1991). These diverse force fields vary substantially in reliability and their deficiencies are reflected in rotational strengths calculated thence. The harmonic force fields utilized in the present calculations are substantially more reliable than any used previously and reduce to insignificance the error in rotational strengths originating from errors in harmonic force fields.

Previous calculations have also adopted a considerable diversity of approaches to the calculation of APTs and AATs. APTs have been calculated ab initio at the SCF level using both derivative methods (numerical [Lowe, Stephens, and Segal 1986; Lowe and Alper 1988] and analytical [Jalkanen et al. 1988, 1990; Kawiecki et al. 1988, 1991; Stephens, Jalkanen, and Kawiecki 1990; Dutler and Rauk 1989; Rauk and Yang 1992; Yang and Rauk 1992; Polavarapu and Bose 1990, 1991]) and sum-over-states methods (Jalkanen et al. 1989; Fablioni et al. 1993). APTs have also been calculated less accurately via fixed partial charge (FPC) (Kawiecki et al. 1991; Stephens, Jalkanen, and Kawiecki 1990), and 'floating basis set vibronic coupling' approaches (Freedman and Nafie 1988). AATs have been calculated ab initio at the SCF level using both derivative methods (numerical [Lowe, Stephens, and Segal 1986; Lowe and Alper 1988] and analytical [Jalkanen et al. 1988, 1990; Kawiecki et al. 1988, 1991; Stephens, Jalkanen, and Kawiecki 1990]) and sum-over-states methods (Jalkanen et al. 1989; Fablioni et al. 1993), and using both common origin (Lowe, Stephens, and Segal 1986; Jalkanen et al. 1990; Kawiecki et al. 1991; Lowe and Alper 1988; Fablioni et al. 1993) and DO gauges (Jalkanen et al. 1988, 1989, 1990; Kawiecki et al. 1988, 1991; Stephens, Jalkanen, and Kawiecki 1990). In addition, AATs have been calculated less accurately via FPC (Kawiecki et al. 1991; Stephens, Jalkanen, and Kawiecki 1990), APT (Kawiecki et al. 1991; Stephens, Jalkanen, and Kawiecki 1990), 'floating basis set vibronic coupling' (Freedman and Nafie 1988), localized molecular orbital (LMO) (Polavarapu and Bose 1990; 1991), and sub-SCF sum-over-states approaches (Dutler and Rauk 1989; Rauk and Yang 1992; Yang and Rauk 1992). The MP2 APTs and semi-MP2 DO gauge AATs used in the present calculations are substantially more accurate than any used previously and considerably reduce the errors in rotational strengths originating in errors in APTs and AATs.

4. CONCLUSION

With the exception of the C-H stretching region of **4** which is strongly perturbed by Fermi resonance, VCD spectra of **1-4** calculated using large basis set MP2 force fields, together with MP2 APTs and semi-MP2 AATs, are in excellent agreement with experiment. Residual errors in frequencies are attributable predominantly to anharmonicity. Residual errors in VCD intensities (rotational strengths) are attributable predominantly to the incomplete inclusion of correlation in the AATs, to anharmonicity and to condensed phase effects. (In the case of calculations at the TZ/2P level, incomplete basis set saturation may also contribute significantly in the C-H and C-D stretching region.) Substantially more accurate calculations require: 1) more complete inclusion of correlation in the calculation of AATs, 2) the inclusion of anharmonicity, and 3) the inclusion of solvent effects. The formalism for the calculation of AATs at the

multiconfiguration self-consistent-field (MCSCF) level using either conventional or field-dependent (London/gauge invariant) atomic orbitals has recently been developed and implemented (Bak et al. 1993). MCSCF calculations of AATs for 1–4, should soon be available and will be of great interest. Hopefully, calculation of AATs using other post-SCF methodologies will also become possible in the near future. The inclusion of anharmonicity in calculations of VCD spectra requires the extension of equations (1b) and (1c) beyond the harmonic level. While well-known for electric dipole transition moments, formalisms for magnetic dipole transition moments including anharmonicity have not yet been developed. Thus, while great progress has recently been made in including anharmonicity in ab initio predictions of vibrational frequencies and electric dipole intensities, analogous calculations of VCD spectra are not yet on the horizon. The study of solvent effects on vibrational frequencies and intensities has a long history. The extension of current, state-of-the-art methods (macroscopic and/or microscopic) to VCD intensities should be straightforward.

Our calculations of the VCD spectra of 1–4 are substantially more accurate than previous work. For the first time, the harmonic force fields used yield frequencies whose deviations from experimental frequencies are due primarily to anharmonicity. The MP2 APTs are substantially more accurate than the APTs used in all earlier work. The combined use of MP2 APTs and large basis set SCF local AATs yield DO gauge AATs substantially more accurate than the AATs used in all earlier work. Comparison of the present calculations and others (past or future) which use specific approximations for force fields, APTs and/or AATs will greatly assist the objective analysis of the relative accuracies of these approximations.

The evaluation of the accuracy of our predicted VCD spectra for 1–4 is substantially limited by the uncertainty of the experimental VCD intensities. This work makes clear the importance of further developments in VCD instrumentation: reliable rotational strengths of well-defined accuracy require substantial improvements in resolution, sensitivity, absolute accuracy, and artifact control. It is to be hoped that the greatly improved capabilities of theory illustrated here will encourage such improvements.

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